



THE COMPOSITION

— OF —

BREDIG GOLD SOLS

DISSERTATION

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Thesis

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THE COMPOSITION OF BREDIG GOLD SOLS.

I. Introduction

"The chief problem of the physics and chemistry of colloids is the study of the structure of the colloid systems," says Svedberg in the opening sentence of a review¹ in October 1924. Further on² he says, "The riddle of the mysterious influence of small—almost undetectable—traces of various substances on the velocity of formation of gold nuclei and on the growth of gold particles is still unsolved." Ever since Graham found³ that ferric and aluminum oxide sols could not be entirely freed from chloride without precipitation, a large amount of work has been done on other hydrosols showing that the presence of a minimum amount of electrolyte is necessary to stabilize the colloid. However, this theory of the complex structure of colloids was restricted to colloids like ferric oxide, since it was generally believed⁴ that suspensoid colloids such as the Bredig gold sols could be prepared in pure water. These sols were believed⁵ to be mechanical suspensions of simple particles in water which did not settle out because of their minute size. According to Duclaux^{5c} for example, a particle 10 millimicrons in diameter would take 16 years to fall 1 cm. under gravity; but since there are opposing tendencies, such as stirring by convection currents as a result of temperature differences, these particles never settle.

Altho it has been generally held that stable Bredig gold sols could be prepared in water, Bredig himself recom-

¹ Svedberg—Chem. Rev. 1, 249 (1924).

² Svedberg—Ibid, p. 258.

³ Graham—Chem. and Phys. Researches, p. 580 (1876).

⁴ Bredig sols preparable in water

a. Bredig—Inaug. Diss. Leipzig, p. 25 (1901).

b. Cassuto (Matula) Der Kolloid Zustand, etc., p. 163 (1913).

c. Duclaux—Les Colloides, p. 17, 19, 20 (1920).

d. Zsigmondy and Spear—Chem. of Coll., p. 93 (1917).

e. Bancroft—B. A. Reports on Coll. Chem. II, 6 (1918).

Applied Coll. Chem., p. 179 (1921).

f. Burton—Phys. Prop. of Coll. Solns., p. 164 (1921).

g. Holmes—Lab. Man. of Coll. Chem., p. 18 (1922).

h. Freundlich—Kapillarchemie, p. 700 (1923).

i. Taylor—Chem. of Colloids, p. 221 (1921).

⁵ Simple Nature of Bredig Sols.

a. Cassuto—ref. 4b, p. 213.

b. Burton—ref. 4f, p. 23.

c. Duclaux—ref. 4c, p. 51.

d. Taylor—ref. 4i, p. 110.

mended^{6a} the use of .001 m. NaOH. Since that time a large number of other colloid chemists have come to the same conclusion⁶—namely, that a slightly alkaline solution is preferable, but that stable sols may be obtained in pure water.

The first important step in the elucidation of the role of the electrolyte was made by Beans and Eastlack in 1915, when they showed⁷ that Bredig gold sols could not be prepared in conductivity water, that is, in water having a specific conductivity of less than 1×10^{-6} mhos. They showed that electrolyte must be present in concentrations ranging from .005 m. to .00005 m.; and that only those electrolytes which contain an anion capable of combining chemically with gold can serve to stabilize these gold sols.

The role played by the electrolyte was further studied in this laboratory by a number of Beans' students. Beaver⁸ found that a certain amount of electrolyte is necessary to stabilize a gold sol prepared by electrical dispersion; that the amount of colloidal gold obtainable is roughly proportional to the amount of electrolyte present; that the negative ion is the active constituent in stabilizing the gold in a gold sol. From conductivity titrations he concluded that the complex between the gold and the anion is destroyed when a sol is precipitated by freezing, but that centrifuging does not destroy the complex. Miller investigated⁹ the maximum amount of colloidal gold obtainable with various concentrations of a number of electrolytes. Briggs studied¹⁰ the relation between degree of dispersion and arcing time, using the centrifuge. Davidson studied¹¹ the stability of gold sols by means of the supercentrifuge. In all of these researches the solutions were made from conductivity water to which definite amounts of electrolyte had been added.

⁶ Electrolyte added

- a. Bredig—Diss. Leipsig, p. 26 (1901).
- b. Bancroft—ref. 4e.
- c. Holmes—ref. 4g.
- d. Ostwald-Fisher—Theoret. and Appl. Coll. Chem., p. 33 (1917).
- e. Zsigmondy—Spear—ref. 4d.
- f. Freundlich—ref. 4h, p. 700.
- g. Duclaux—ref. 4c.
- h. Whitney and Blake—J. A. C. S. 26, 1376 (1904).

⁷ Beans and Eastlack—J. A. C. S. 37, 2667 (1915).

⁸ Beaver—Dissertation, Columbia, 1921.

⁹ Miller—Dissertation, Columbia, 1922.

¹⁰ Briggs—Dissertation, Columbia, 1923.

¹¹ Davidson—Dissertation, Columbia, 1924.

As a result of the preceding researches there can be absolutely no question regarding the validity of the conclusions drawn by Beans and Eastlack in 1915; namely, that stable gold sols cannot be prepared in water; that electrolyte must be present in concentrations between certain limits; and that the electrolyte must contain an anion capable of combining chemically with gold. All these facts indicated quite strongly that the reason gold dispersions were stable in certain concentrations of certain electrolytes was because the gold particles formed a complex by combining in some manner with the anion.

It was in the hope of obtaining direct evidence of the formation of a complex that this research was undertaken. It was planned to obtain the concentration of chloride ion in a dilute KCl solution by means of electromotive force measurements; to arc for varying lengths of time in other portions of this same KCl solution, and then to measure the emf of the cells using these sols in place of the original KCl solution. Thus, the changes in chloride ion concentration consequent to formation of sol could be studied, provided of course, that such potential measurements in the sol could be made.

II. Materials and Apparatus

The KCl used was C. P. KCl recrystallized three times from conductivity water, dried and fused in a platinum dish, pulverized in an agate mortar and kept in a dessicator. All solutions were made up in doubly distilled water having a specific conductivity varying between 0.9 and 1.2×10^{-6} mhos. The solutions were all kept in non-sol bottles, which had been cleaned, steamed and dried. The beakers and cells used were all of pyrex glass. The conductivity and potential measurements were made in a water thermostat maintaining a temperature of 25.00 ± 0.02 C. The Beckmann thermometer used was compared with a standard thermometer certified by the U. S. Bureau of Standards. The weights and flasks used were all calibrated.

The instruments used were a Leeds and Northrup Type K potentiometer, a high sensitivity galvanometer, a Weston standard cell, and a Leeds and Northrup conductivity set up with a Vreeland oscillator.

The working standard cell was checked at intervals with a standard Marion Eppley cell No. 8246, and was found to give a value of 1.0187 volts which did not change. The arcing apparatus and centrifuge were the same as described by Briggs. The current was maintained at $3.3 \text{ amps} \pm 0.3 \text{ amp}$.

III. Preliminary Investigation

For measuring the activity of chloride ions at low concentrations, the silver chloride electrode has been found more satisfactory than the calomel. Silver chloride electrodes were used by Goodwin,¹² by Jahn,¹³ and by Halla.¹⁴ MacInnes and Parker¹⁵ used gauze electrodes. They found on comparing at random, electrodes made at different times, that they checked to a few tenths of a millivolt. Lewis, Brighton and Sebastian¹⁶ used the method of MacInnes and Parker, and found that they gave constant, but not always reproducible potentials. The thermodynamic properties of the AgCl so produced vary with the method of preparation. Lewis and his co-workers found that in dilute solutions the silver chloride electrode comes more quickly to equilibrium and shows greater constancy than the calomel. But since the AgCl electrode was not always reproducible, they established the value of a particular AgCl electrode by comparison with a calomel electrode, and then used the AgCl electrode as a reference. Noyes and Ellis¹⁷ used AgCl electrodes made by decomposing silver oxide with heat, and coating the resulting porous silver with AgCl. They too found the AgCl electrodes to give more reliable results with dilute chloride solutions than did the calomel electrodes; but according to the authors, even the former failed when the chloride concentration reached 0.0003 m., and at 0.001 m. they were, perhaps, unreliable. Linhart claimed¹⁸ results of high precision with the AgCl electrode. In all previous investigations, he states, measurements in solutions as dilute as 0.01 m. have been subject to slight uncertainty, and at higher dilutions they have proved unreliable. By using his method, he states that he obtained results of high precision nearly to a concentration of 0.0001 m. MacInnes and Beattie following the original method of MacInnes and Parker obtained¹⁹ much more constant and reproducible electrodes than in the previous work. However .001 m. was the most dilute solution for which they gave results.

¹² Goodwin—Z. phys. Ch., 13, 630 (1894).

¹³ Jahn—Z. phys. Ch., 33, 556 (1900).

¹⁴ Halla—Z. Elektroch. 17, 179 (1911).

¹⁵ MacInnes and Parker—J. A. C. S. 37, 1449 (1915).

¹⁶ Lewis, Brighton and Sebastian—J. A. C. S. 39, 2252 (1917).

¹⁷ Noyes and Ellis—J. A. C. S. 39, 2533 (1917).

¹⁸ Linhart—J. A. C. S. 41, 1175 (1919).

¹⁹ MacInnes and Beattie—J. A. C. S. 42, 1118 (1920).

Since the concentration of electrolyte necessary for stabilization of sols is low—ranging from .00005 m. to .005 m.—and since Linhart was the only one who claimed results of high precision at low concentrations, his method was selected as the one most likely to give satisfactory results.

Considerable time and effort were spent in trying to obtain results with this method. A large number of variations were tried, but the method finally had to be given up. Altho electrodes of this kind prepared in the same manner often checked to 0.1 or 0.2 mv. in KCl, yet in a number of cases electrodes prepared apparently identically differed by 0.6 to 1.0 mv. and sometimes more. In sols the results were entirely unsatisfactory as the emfs were neither constant nor reproducible. However, with but one exception the emfs obtained with sols using a Ag—.01m AgNO₃ reference electrode were less than that obtained with the solution before arcing, indicating a chloride ion decrease. Fresh electrode material was used for each experiment.

The results so far obtained may be summarized by the statement that this form of electrode was not very satisfactory in KCl solutions and quite unsatisfactory in gold sols, but that there appeared to be a decrease in chloride ion concentration subsequent to arcing.

IV. Apparatus Used.

Altho in the hands of this investigator Linhart's silver chloride electrode did not give satisfactory results, it was decided to try another form of silver chloride electrode before abandoning this method of attacking the problem.

A number of electrodes were made up following the method of MacInnes and Parker, and of MacInnes and Beatrice. After bringing them to equilibrium with the solution to be measured they were all put into one beaker containing that solution and the P. D. between them was measured. They agreed for the most part to 0.1 mv. and in no case differed by more than 0.3 mv. A sol was then made with another portion of that solution and the electrodes put into the sol. The widest difference was 0.2 mv. They were then put back into the original solution and again they agreed to 0.1 mv—the widest difference being 0.2 mv.

Since the results obtained with this kind of electrode looked promising a cell was set up using as a reference half-cell one of these silver chloride electrodes in a .005 m. KCl solution. The advantages of such a reference half-cell are several. In the first place, it keeps constant according to

Lewis, Brighton and Sebastian. In the second place, since the electrodes and solutions in the two half-cells are identical, the cause of any changes in potential obtained after arcing will be restricted to the effect of the solution on the electrodes, and there will be ruled out any possibility of P.D. due to differences in the electrodes. In the third place the flowing junction²⁰ can now be used since .005 m. KCl will not precipitate the gold sols used in the other half-cell. Thus there are eliminated the uncertainties connected with liquid junction potentials.

A number of cells were designed and used. In its final form the cell had the dimensions given in Fig. 1. As stated previously the cells were entirely of pyrex glass, with the exception of the electrode holders which did not come in contact with the solution. The cell was made in five pieces so as to facilitate cleaning and render manipulation easier. Rubber tubing held the glass ends in close contact. All joints were sealed with paraffin.

V. Method of Procedure

The Cell

The cell was thoroughly cleaned, then steamed and dried. A, B and D (Fig. 1) were connected together and rinsed several times with .005 m. KCl. This reference half was then clamped in place, and the electrodes H, prepared as described below, put lightly into place. The bulb D was filled with .005 m. KCl, the rubber tubing at M was pinched closed, the stopcock F was opened, the solution was permitted to fill A up to the point "a," and then the stopcock F was closed. The stopper H was now set in firmly, and the ground glass joint was paraffined.

C and E were then fastened in place after first rinsing with .001 m. KCl, and the bulb E filled with that solution. The stopcock G was opened, the solution permitted to fill C up to the point "b," and the stopcock G closed. The electrodes K were then put in and the ground glass joint sealed with paraffin.

The two half cells were then connected at M and the joint sealed with paraffin. The entire cell was lowered into the thermostat for 15 min. then it was lifted up, the stopcock O

²⁰ Lamb and Larson—J. A. C. S. 42, 229 (1920).

FIG. 1

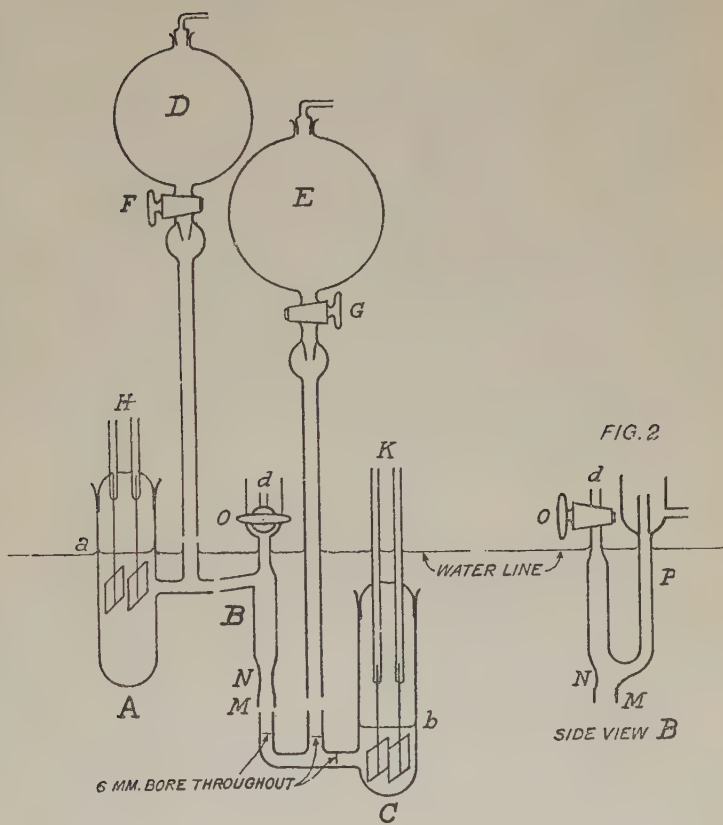
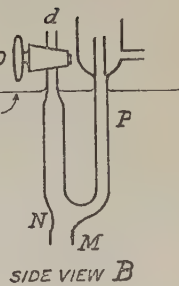


FIG. 2



was opened wide, and the stopcock G was opened so that the dilute solution dripped rather slowly. Since the half cell was air-bound, the level could not rise above "b"; the solution therefore rose in the tube B. When the level reached the exit tube at N, the stopcock F was opened wide and the reference solution flowed into B, made junction with the other solution at N and flowed up to "d". The stopcock O was then closed, the drip at F was made slower and the mixed solution flowed out thru the exit tube P. Then the drip at both F and G was adjusted to about one drop every five seconds, the cell lowered into the thermostat and readings taken.

In every solution and every sol measured there were two electrodes. The potential difference between the two reference electrodes was checked at intervals during each experiment. They usually differed by no more than 0.1 or 0.2 mv.

Then the P.D. was measured between one of the reference electrodes and each of the electrodes in the other half cell. Readings were taken at intervals of about five minutes. At the conclusion of the experiment the cell was disconnected at M, and the stopcocks F and G were closed. The reference half was left undisturbed.

The Electrodes.

The electrodes were made by sealing into soft glass a platinum wire and welding on it a platinum gauze. The electrodes were then heavily plated with silver, washed, and then coated with silver chloride by electrolysis in potassium chloride solution. This last step was carried out in solutions ranging from 0.05 to 0.1m. The electrodes were then washed with a stream of distilled water, and let stand in a beaker of the solution to be measured. Next they were washed with a forceful fine stream of the same solution by means of small wash bottles of 15 cc. capacity. Usually about 30 cc. of solution were used. The electrodes were then put into their place in the cell. After standing five minutes, they were used to stir the solution in the cell and were finally fixed firmly in place.

These electrodes lasted for varying lengths of time. Some of them were spoiled by precipitation of gold upon them. Some of them exhibited the white spots mentioned by MacInnes and Parker, and some of them seemed to grow a fine fuzz which may have been the bacterial growths observed by these authors. The electrodes were good for about from three to ten experiments. Those left undisturbed in the reference half cell lasted often for weeks.

A number of methods of removing the chloride coating were tried. The method finally adopted for renewing the electrodes consisted of dipping the electrodes in a hot concentrated NH_4Cl solution²¹ for two or three minutes, rinsing off the NH_4Cl , and holding the gauze above a small Bunsen flame until it glowed with a delicate rosy tint. Care must be taken not to get the gauze too hot or the silver will fuse. If the gauze glows with a yellow color instead of a pink one, repeat the NH_4Cl treatment to remove the fused AgCl . After the flame treatment, dip the electrodes into the hot NH_4Cl solution again, and rinse with water. It can now be coated with AgCl immediately. In this way a spoiled electrode can be cleaned and recoated within half an hour.

On several occasions freshly made electrodes were "dead." No current was obtained from the cell even when the potentiometer setting was considerably off balance. The electrodes looked normal. A number of expedients were tried. Finally successful results were obtained by connecting leads from a 60 cycle AC generator with the dead electrodes, and current passed for one minute. This treatment brought them to life. Perhaps too complete a coating of silver chloride had rendered the electrodes non-conducting; the AC probably dissolved off and reprecipitated the AgCl , leaving the electrodes in a conducting state.

All solutions used were made by weighing out a calculated amount of KCl and adding 3 liters of conductivity water. After measuring the emf of the cell with one portion of KCl , another portion of the same dilute solution was set into the arcing apparatus and arced for a definite length of time. The time of arcing was taken as the actual time during which the arc burned. The solution was cooled by a mixture of ice and water, the maximum temperature usually being 30°C .

When the sol was made, a small wash bottle, the half cell C and the bulb E (see Fig. 1) were rinsed three times with small portions of the sol. E and C were connected and clamped in place. About 50 cc. of sol was put into E, G was opened and sol let flow into C to the level "b." It is important to introduce the sol in this way as otherwise an air bubble may form in the arm and cause a break in the circuit. The pair of electrodes was washed with 30 cc. of sol and put into the half cell as was done with the KCl solution. From this point on the procedure was the same as for the KCl solution.

The junction between the two solutions was fortunately very easily observed, since the sol was red. In all cases a

²¹ Mellor—Inorg. and Theor. Chem., III, 400 (1923).

sharp line of demarcation was obtained between the sol and the reference solution extending even up the exit tube P. (Fig. 2.)

At the end of an experiment, the electrodes were taken out of the sol, rinsed with water and let stand in a beaker of the KCl used. About 60 cc. of the sol were then put into a clean pyrex centrifuge tube and centrifuged for 30 min. at about 1200 times gravity. For analysis, 25 cc. of sol was pipetted off, precipitated with a few drops HCl, filtered thru a Gooch crucible, ignited and weighed.

VI. Results.

The first cell set up was



The emf of this cell was measured. Then 250 cc. of the KCl solution was arced for 5 minutes and put into one half cell, leaving the other half cell untouched to serve as a reference. The emf was measured, the cell cleaned again, and another sol put in, etc. The results are given in Table I.

TABLE I.—0.005 m. KCl.

Solution Used.	Volume Arced.	Arcing Time.	E. M. F. Observed.
.005m. KCl	-----	0 min.	0 mv
Sol No. 1	250 cc	5 "	2 "
Sol No. 2	" "	15 "	2 "
.005 m. KCl	-----	0 "	0 "
Sol No. 3	250 cc	15 "	3 "
Sol No. 4	" "	30 "	5 "
.005 m. KCl	-----	0 "	1 "
.005 m. KCl	-----	0 "	0 "
Sol No. 5	250 cc	30 "	*2 "
Sol No. 6	" "	58 "	10 "
Sol No. 7	" "	80 "	†12-16 "
Sol No. 8	" "	30 "	3 "
Sol No. 9	" "	30 "	3 "
Sol No. 10	" "	30 "	6 "
.005 m. KCl	-----	0 "	2 "
.005 m. KCl	-----	0 "	0 "

*Stood 2 days before measuring.

†Unsatisfactory readings. Electrodes were found to be covered with gold.

Leaving the reference half cell untouched, similar experiments were conducted using .001 m. KCl instead of .005 m. KCl in the other half cell. As in the first series, the emf of the concentration cell using KCl only, was repeatedly determined as a check upon the electrodes and the reference half cell. The results are given in Table II.

TABLE II—0.001 m. KCl.

Solution Used.	Volume Arced.	Arcing Time.	E. M. F. Observed.	Δ E.M.F.
.001 m. KCl	-----	-----	40 mv	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
Sol No. 11	250 cc	15 min.	44 "	4 mv
Sol No. 12	250 cc	15 min.	40 mv	3 mv
Sol No. 13	" "	15 "	40 "	3 "
.001 m. KCl	-----	-----	37 "	-----
.001 m. KCl	-----	-----	37 "	-----
Sol No. 14	250 cc	30 min.	40 "	3 mv
Sol No. 15	250 cc	30 min.	44 mv	4 mv
Sol No. 16	" "	60 "	46 "	6 "
.001 m. KCl	-----	-----	41 "	-----
.001 m. KCl	-----	-----	40 "	-----
Sol No. 17	250 cc	90 min.	49 "	9 "
Sol No. 18	" "	120 "	53 "	13 "
Sol No. 19	" "	120 "	58 "	18 "
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	42 mv	-----
.001 m. KCl	-----	-----	42 "	-----
.001 m. KCl	-----	-----	43 "	-----
.001 m. KCl	-----	-----	43 "	-----
Sol No. 20	250 cc	60 min.	49 "	6 mv
Sol No. 21	" "	90 "	57 "	13 "
.001 m. KCl	-----	-----	44 "	-----
.001 m. KCl	-----	-----	43 "	-----
.001 m. KCl	-----	-----	43 "	-----
Sol No. 22	250 cc	90 min.	55 "	12 mv
Sol No. 23	" "	120 "	62 "	19 "
Sol No. 24	200 "	120 "	64 "	20 "
.001 m. KCl	-----	-----	44 "	-----
.001 m. KCl	-----	-----	43 "	-----

When it was found that there was an unmistakable increase in emf subsequent to arcing, and that it might be possible to secure quantitative instead of merely qualitative data, a new cell was designed in the hope of increasing precision. And since potential measurements were successful even in sols that had been arced 8 hours per liter—a result which had hardly been expected—the experiments were carried on with more concentrated sols. However, to reduce the tedious task

of arcing, the volume taken for arcing was cut down to 200 cc. The series was begun again from the beginning. The data is given in Table III.

TABLE III—0.001 m. KCl (New Cell)

Solution Used.	Volume Arced.	Arcing Time.	E. M. F. Observed.	Δ E.M.F.
.001 m. KCl	-----	-----	40 mv	-----
.001 m. KCl	-----	-----	41 "	-----
Sol No. 25	200 cc	45 min.	49 "	9 mv
Sol No. 26	" "	45 "	52 "	12 "
.001 m. KCl	-----	-----	42 "	-----
.001 m. KCl	-----	-----	39 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
Sol No. 27	200 cc	60 min.	*54-56 "	14-16 mv
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----
Sol No. 28	200 cc	90 min.	†51 "	11 mv
Sol No. 29	" "	60 "	52 "	12 "
Sol No. 30	" "	180 "	73 "	33 "
Sol No. 31	" "	223 "	72 "	32 "
Sol No. 32	" "	240 "	70 "	30 "
.001 m. KCl	-----	-----	40 "	-----
.001 m. KCl	-----	-----	40 "	-----

*Readings unsteady; electrodes were found to be spoiled.

†Stood 15 days before measuring.

Sol No. 31 was found to contain 3.8 gm. gold per liter.

Sol No. 32 was found to contain 3.3 gm. gold per liter.

Concentration 0.0008 m. KCl

The technique had now been improved to the point where results of precision were being obtained. It was therefore decided to analyze each sol for its gold content. From the results already obtained it was seen that in general the observed emf for KCl solutions was within 1 mv. of the calculated value. Whenever, therefore, a set of electrodes in KCl in the succeeding experiments differed from the calculated value by more than 1 mv. it was not used for measurement in sols. Occasionally it was found that the fault lay with the set of reference electrodes. To insure against errors due to change in the electrodes, as well as to test the newly coated electrodes, it is important to measure at frequent intervals the emf of the cell using only known KCl solutions. In the following tables such test experiments are not given, but it is to be understood that they have been made. Results obtained at this concentration are given in Table IV and graphically by Curve I.

TABLE IV—0.0008 m. KCl

Solution Used.	Volume Arced.	Arcing Time.	Observed E.M.F.	Δ E.M.F.	Gold content per liter.
0.0008 m. KCl			46 mv		
Sol No. 33	250 cc	45 min.	53 "	7 mv	0.7 gm
Sol No. 34	200 "	60 "	56 "	10 "	1.0 "
Sol No. 35	200 "	120 "	68 "	22 "	2.0 "
Sol No. 36	200 "	180 "	78 "	32 "	2.9 "
Sol No. 37	200 "	238 "	87 "	41 "	3.4 "
Sol No. 38*	200 "	255 "	92 "	46 "	3.5 "
Sol No. 39	200 "	300 "	98 "	52 "	3.7 "
Sol No. 40	200 "	360 "	109 "	63 "	3.8 "

*A new cell was here designed and made which was in many respects better than the previous ones. It is this third cell that is given in Fig. I.

After arcing 10 hours per liter at .0008 m. it was expected that each succeeding point would show a break in the curve. The curve however continued as a straight line. Since this was quite different from results at .001 m., it was decided to repeat the experiments at .001 m. to make sure whether or not there was such a difference in behavior at the two concentrations. The following measurements were made using the newest cell. Results are given in Table V and by Curve IV.

TABLE V—0.001 m. KCl

Solution Used.	Volume Arced.	Arcing Time.	Observed E.M.F.	Δ E.M.F.	Gold content per liter.
0.001 m. KCl			40 mv		
Sol No. 41	200 cc	60 min.	50 "	10 mv	1.0 gm
Sol No. 42	200 "	120 "	62 "	22 "	1.6 "
Sol No. 43	200 "	180 "	72 "	32 "	2.65 "
Sol No. 44	200 "	240 "	84 "	44 "	3.4 "
Sol No. 45	100 "	150 "	92 "	52 "	4.2 "
Sol No. 46	100 "	180 "	79 "	39 "	4.1 "
Sol No. 47	100 "	210 "	87 "	47 "	4.1 "
Sol No. 48	250 "	60 "	47 "	7 "	*

* Not analyzed.

Electrolysis.

To see whether electrolysis of chloride occurred, blanks were run by permitting the current to pass thru the solution, but without arcing. Bubbles of gas were evolved at both electrodes. After some time the emf was measured and showed an increase.

Since the P.D. across the electrodes is 25 to 30 volts, and since there is no liquid in contact with the hot tips of the electrodes during arcing, the blanks subsequently were so run as to

duplicate as far as possible electrolysis conditions existing while arcing was going on. The tips of the electrodes were therefore coated with paraffin, and the P.D. was adjusted to 25-30 v. Under these conditions the current was about 0.008 amps. The results at .0008 m. KCl are given in Table VI.

TABLE VI.

Solution Electrolyzed.	Time.	Observed E.M.F.	Volume
1. 0.0008 m. KCl	0 min.	46 mv	-----
2. " " "	60 "	58 "	100 cc
3. " " "	120 "	67 "	100 "
4. " " "	192 "	83 "	100 "

These results are given graphically by Curve III.

Since no chlorine had been detected by previous investigators in the escaping gases, and since there was an indubitable decrease in chloride ion, the solutions were tested with KI and starch suspension. The solutions all gave positive reactions, the longer electrolyzed ones giving a more marked color, showing the presence of oxidation products of electrolyzed chloride.

Since these points lay on a straight line no more blanks were run at this concentration.

At .001 m. KCl, the blanks first obtained did not increase regularly with time of electrolysis. To see whether the marked deviations were due to experimental error, a large number of blanks were made. The results are given in Table VII.

TABLE VII.

Solution Electrolyzed.	Volume.	Time.	E. M. F. Observed
a. 0.001 m. KCl	-----	0 min.	40 mv
b. " " "	250 cc	60 "	40 "
c. " " "	100 "	60 "	42 "
d. " " "	" "	120 "	52 "
e. " " "	" "	180 "	64 "
f. " " "	" "	93 "	57 "
g. " " "	" "	150 "	50 "
h. " " "	" "	210 "	56 "
i. " " "	" "	120 "	58 "

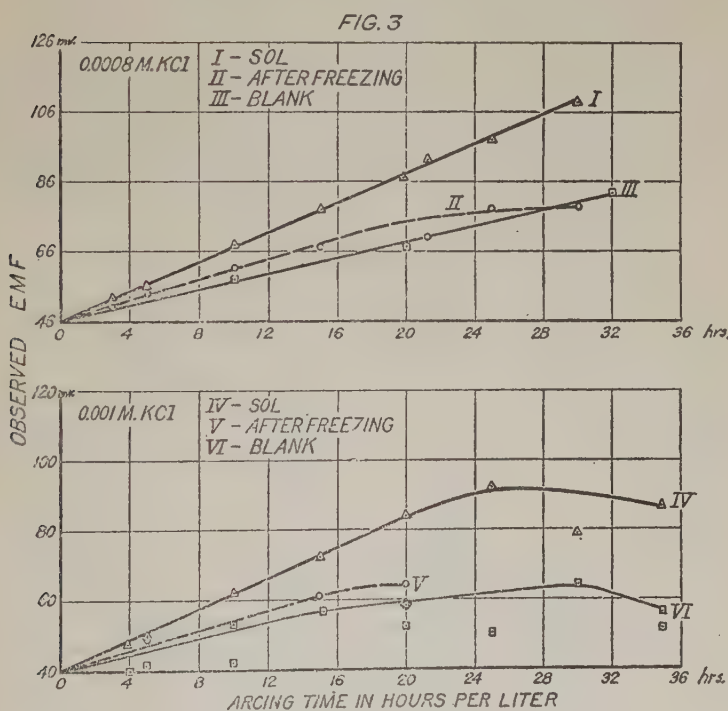
Blank "b" was set up in parallel with another identical solution which was arced for 60 minutes. In this way the

P.D. across the electrodes in the blank and in the sol was always identical. This sol, No. 48, gave an emf of 47 mv which is on the sol curve, whereas the blank gave 40 mv. On testing with KI and starch, a negative reaction was obtained, thus checking the emf results.

To make sure that the paraffin did not cause these irregularities, the paraffin was removed, and blanks then run. The results are given in Table VIII.

TABLE VIII.

Solution Electrolyzed.	Volume.	Time.	Observed E. M. F.
j. 0.001 m. KCl	-----	0 min.	40 mv
k. " " "	100 cc	30 "	41 "
l. " " "	" "	60 "	56 "
m. " " "	" "	120 "	58 "
n. " " "	" "	210 "	51 "



After measuring "l", the electrodes on being tested gave 43 mv instead of 40 mv, giving therefore a Δ E.M.F. of 13 mv. The results for .001 m. KCl blanks are given on Fig. 3.

Solution "k" was tested chemically. It gave no color thus confirming the emf measurements. The points are irregularly located, but the maximum amount electrolyzed may be considered as given by a curve connecting the highest points. Curve VI has been so drawn as to connect the highest points.

Freezing Experiments.

In those experiments where there remained sufficient sol for another emf determination, the sol was put into a clean non-sol bottle, tightly stoppered and frozen in the refrigerator at about -5° C. When frozen, the ice was colorless²². The ice was then melted, the solution was stirred by shaking, and then put into the thermostat to attain the desired temperature. The solution was put into the cell and the emf measured exactly as described for the sols.

With some of the more concentrated sols freezing once did not completely precipitate the sol. The ice was colored pink in spots. In these cases the ice was melted and the sol put back again in the refrigerator. A second freezing served to completely decolorize the sol, showing complete precipitation. Table IX and Curves II and V give the results of those sols that were frozen.

TABLE IX.

Sol.	Gold Content.	0.0008 m. KCl sols.		E.M.F. after freezing (c)	(c-a)
		E.M.F. .0008 m. KCl (a)	E.M.F. sol. (b)		
No. 33	0.7 gm/liter	46 mv	53 mv	50 mv	4 mv
No. 34	1.0 " "	46 "	56 "	54 "	8 "
No. 35	2.0 " "	46 "	68 "	61 "	15 "
No. 36	2.9 " "	46 "	78 "	67 "	21 "
No. 38	3.5 " "	46 "	92 "	70 "	24 "
No. 39	3.7 " "	46 "	98 "	78 "	32 "
No. 40	3.8 " "	46 "	109 "	79 "	33 "

Sol.	Gold Content.	0.001 m. KCl sols.		E.M.F. after freezing (c)	(c-a)
		E.M.F. .001 m. KCl (a)	E.M.F. sol. (b)		
No. 41	1.0 gm/liter	40 mv	50 mv	49 mv	9 mv
No. 43	2.65 " "	40 "	71 "	61 "	21 "
No. 44	3.4 " "	40 "	84 "	64 "	24 "

²² Zsigmondy—Kolloidchemie, p. 66 (1912).

Curve IX gives the relation between gold content and observed emf before freezing and Curve X after freezing, at .0008 m. For .001 m. similar curves are obtained.

Effect of Centrifuging.

To see whether centrifuging affected the emf, the sol remaining after the original measurement was made, was centrifuged for 30 minutes at about 1200 times gravity. Two experiments were made; sol No. 32 which gave 70 mv, after centrifuging gave 75 mv; sol No. 37 which gave 87 mv, after centrifuging gave 98 mv. In both cases there was a decided increase in emf, showing that the gold thrown out on centrifuging adsorbs additional electrolyte. This effect was not studied further.

Changes on Standing.

Very few of the sols gave a constant emf. The emf rose rapidly for the first 10 minutes and then slowly drifted, usually up. Sometimes it reached a maximum and began drifting down. In other cases it drifted up and down within two millivolts of an average value. Since this was the case, and since it was not known in advance what the effect of time would be, the sols were measured a short time after being made. They were put into the cell from 30 minutes to 2½ hours after the arcing was ended, were given 15 minutes to attain the desired temperature; and then readings were taken over a period of about 30 minutes after that.

Some sols were left in the cell for days and the emf read at intervals. In a few cases the emf remained the same; in a few it increased; in others however the emf decreased markedly. The results are given in Table X.

TABLE X.

Sol.	Time Elapsed.	Original E.M.F.	Final E.M.F.
No. 5	2 days	(5) mv	2 mv
No. 6	1 "	10 "	6 "
No. 9	1 "	3 "	5 "
No. 11	1 "	44 "	39 "
No. 18	1 "	53 "	58 "
No. 25	1 "	49 "	50 "
No. 26	1 "	52-53 "	52 "
No. 28	15 "	(57) "	51 "
No. 38	1 "	92 "	83 "

Sol No. 5 and No. 28 were measured only after they had stood for some time. The values for the original emf given in parenthesis are the expected values for them obtained from the curves.

A typical set of readings is given in Table XI. K and L are the electrodes in the reference solution and O and P the electrodes in the sol.

TABLE XI.—Sol No. 40.

E.M.F. bet. Reference Electrodes K and L set electrodes in sol	E. M. F. of cell		Time	
	K and O	K and P	put cell in thermostat	P. M.
—0.11 mv				8:30
—0.12 “				8:35
	107.5 mv	108.0 mv		8:36
	108.6 “			8:50
	108.5 “	108.5 “		8:54
—0.13 “	108.8 “	109.3 “		8:55
	95.0 “	109.3 “		9:04
	109.1 “	109.2 “		9:13
—0.12 “	109.1 “	109.1 “		9:15
				9:25

The anomalous value of 95.0 mv was not exceptional. On a number of occasions the emf obtained in the course of an experiment was excessively high or low. If a slight amount of current is allowed to flow, the potential comes back to normal—to the equilibrium value. This apparently is the same phenomenon mentioned by Clark.²³ Permitting a small amount of current to flow thru the cell by setting the potentiometer slightly out of balance brings the emf back to the true equilibrium value.

Electrical Leakage.

No trouble was experienced with electrical leaks most of the time. On a few occasions the emf was low and erratic. Instead of using an oil thermostat as recommended by many investigators, simple coating with paraffin of the parts of the cell in the water gave immediate and satisfactory elimination of leakage.

Note.

It is emphasized here that these sols for which data has been given, are not selected sols. Forty-eight sols were made from the time when the first measurement was made with gauze electrodes. All have been recorded here, and none has been omitted.

VII. Discussion.

As was stated in the introduction, it is still generally believed that Bredig gold sols can be prepared in water despite the fact that the results of Beans and Eastlack have been available since 1915. It is by now generally realized that satisfactory results are not always obtained by the use of “water”, and so dilute sodium hydroxide solutions are often recommended. (6a, b, c, e, f, g) Whitney and Blake used a dilute HCl solution also. The part played by electrolytes remained

²³ Clark—Determination of Hydr. Ions. p. 210 (1923).

obscure as can be seen for example from the fact that Ostwald ^(6d) added a trace of bicarbonate of soda in order to obtain a stable gold sol. Duclaux stated ^(6g) that if the sol is violet or blue, it is because the water used was not pure enough or the current was too high, altho Bredig got ^{4a} poor results in water with low current, and better results with high current. Holmes says ^(6c) if the sol obtained is blue, try heating to see if it turns red.

Beans and Eastlack showed that only those salts whose anions were capable of combining chemically with gold could serve to stabilize gold sols. Beaver confirmed these findings. He found that the chloride ion concentration decreased as a result of the production of the sol. Altho he did not differentiate between chloride ion lost by adsorption and that lost by electrolysis, yet he found that freezing destroyed the complex and liberated chloride ion, and that centrifuging did not. He also found that the amount of gold present as colloid was a function of the electrolyte concentration. Studying this in detail, Miller found that the maximum quantity of gold obtainable was a function not only of the concentration, but also of the electrolyte. With the same concentration of KCl, KBr, and KI, the maximum amount of colloidal gold obtainable in each decreases in that same order. In other words, the adsorption is apparently not a mere mechanical adsorption, but a chemical combination of some sort between the gold particle and the anion. Aurous or auric gold ions do not appear to be involved in this reaction since tests for ionic gold have always been negative. In this laboratory on several occasions a large volume of sol was precipitated, concentrated to a small volume and tested with alkaline H_2O_2 , with negative results. This reagent quantitatively precipitates gold in concentrations as low as .03 mg in 10cc. Adolf and Pauli²⁴ found that traces of gold, dissolved or suspended, caused the hydrogen electrode to give erratic results. Since the supernatant liquid after the coagulation of a formaldehyde sol permits of obtaining constant results with the hydrogen electrode, they concluded that gold ions were not present in the solution. As yet this delicate test has not been applied to Bredig sols, but there is no reason to expect that Bredig sols will show ionic gold when a sol prepared from auric chloride does not. Moreover, if ionic gold is the important factor, why cannot sols be obtained in conductivity water?

From the data obtained in this investigation it is seen that altho the chloride ion concentration decreases because of electrolysis, yet the amount lost in this manner is less than the decrease consequent to formation of sol. This difference

²⁴ Adolf and Pauli—K. Z., 34, 29 (1924).

is too great to be accounted for by experimental error. It has consequently been interpreted as the amount of chloride ion disappearing to form the adsorption complex. That this conclusion is correct is borne out by the fact that on precipitating the sols by freezing the concentration of chloride ion increases. Inasmuch as no electrolyte had been added, and inasmuch as the only treatment of the solution had been a moderate lowering and a raising of temperature, the other equilibria could not have been affected. Consequently this increase of chloride ion must have come from the decomposition of the adsorption complex. Moreover, as can be seen from Fig. 3, the freezing curves are above the electrolysis curves, showing that altho the complex has been broken and chloride ion liberated, yet all of the chloride ion does not reappear. This has been interpreted to mean that some of the chloride ion has been carried down by the precipitated gold.

The values when plotted give curves which, when the complicating factors are taken into consideration, are of satisfactory regularity. In the first place it may be pointed out that the points on the curves each represents an independent experiment. Emf readings were not made at intervals on the same sol or even on separate portions of the same sol or electrolyzed solution. A fresh portion of KCl solution was taken in each case, treated as indicated, and then measured. In view of the sensitivity of gold sols and the hypochlorite equilibrium to a number of factors such as light, solution of atmospheric gases, etc., and in view of the fact that the arcing and electrolyzing continued for many hours, the regularity obtained is quite satisfactory in most cases. In two cases the results obtained are puzzling.

The two sets of values for .001 m. sols check up to 15 hours per liter. After that time if all the results were plotted together, there would be three points off the curve and three on the curve. This was at first attributed to experimental error—for instance permitting chloride impurity in minute amount to enter the sol. On Curve IV one point is off the curve, the difference is potential between this and the next point being 8 mv. Now a difference of emf from 79 to 87 mv for this cell corresponds to a difference in chloride ion concentration of 0.00006 m. In a concentration cell 0.1—0.5 m., such a difference in concentration would not have an appreciable effect. It is thus evident how easily minute quantities of impurity can throw out results such as these. However, when we examine the blanks for .001 m. KCl, we see that here again the degree of reproducibility and the regularity are not all that might be desired. Apparently then, the irregularities observed in .001 m. sols are not due to impurities but to irregularities occurring in the electrolysis.

If that is the case, it seems strange that similar irregularities were not observed with the .0008 m. sols and electrolysis blanks. The regularity of Curve III may be only apparent, due to the fact that only three experiments were run and that these happened to be on a straight line with the origin. It seems, however, that if irregularities existed, they would have appeared in Curve I or Curve III. Six experiments were made at .0008 m. longer than 15 hours per liter, and not a single irregularity is evident.

Curves VII and VIII give the change in gold content with time of arcing. The two curves run along together up to 20 hours per liter. After that Curve VII flattens out. Curve VIII runs up higher before flattening out. This agrees excellently with the results of Briggs and Davidson. They concluded on the basis of centrifuging experiments, that the number of particles increased up to a certain point. After that, continued arcing did not increase the number of particles, but served only to increase the size of the particles. These particles being heavier, were more easily thrown out by centrifuging. Consequently, after arcing for some time, the slope of the curve decreases. With increasing concentration up to an optimum there are more particles formed and there, therefore, is a higher gold content at higher concentrations. Curves VII and VIII are in accord with these conclusions.

It had been hoped that data would be procured from which could be made a precise calculation of the number of chloride ions adsorbed. Because of the complications introduced by electrolysis, the values calculated here are subject to uncertainty. Nevertheless it is interesting to see what these values are.

In order to get more certain values, it will be necessary to eliminate electrolysis of chloride ion. A few preliminary experiments on dilute KCl solutions using the condensed spark gave excellent results. One sol, sparked for 10 hours per liter, after precipitating the sol and filtering gave no reaction with starch and KI. This line of investigation is now being followed up in this laboratory. In addition, similar work is being planned on Bredig hydroxide sols. Decrease in hydroxyl ion concentration in such sols consequent to arcing will be due to adsorption alone, as electrolysis will not change the pH.

From the results obtained here the number of gold atoms per chloride ion has been calculated as follows:

From Curve I $\Delta E.M.F. = 2.1$ mv per hour for electrolysis and adsorption.

From Curve III $\Delta E.M.F. = 1.1$ mv per hour for electrolysis alone.

Therefore $\Delta E.M.F. = 1.0$ mv per hour for adsorption alone.

On the assumption that the observed changes in emf are due to decreases in chloride ion concentration, the chloride ion concentration in each sol has been calculated from Nernst's formula, using data obtained from Lewis and Randall.²⁵

The emf of the cell



was first calculated for different values of m' (molarity) from the formula

$$\text{E.M.F.} = 59 \log \frac{a_{.005}}{a_{m'}} \text{mv}$$

where a is the activity of the chloride ion.

A curve was then drawn on a large scale giving the relation between the activity of the chloride ion and the emf obtainable. From this activity-emf curve the chloride ion activities corresponding to given emfs were obtained and used in the following calculations.

Using the rate of change in emf due to adsorption alone as 1.0 mv per hour, the amount of chloride ion adsorbed has been obtained and is given in Table XII.

TABLE XII.

At end of	Π	$a \times 10^3$	At end of	$\Delta + \Delta \Pi$	$(a + \Delta a) \times 10^3$	$\Delta a \times 10^3$	dur- ing.
0 hr.	46.0 mv	0.784	1st hr.	47.0 mv	0.760	0.024	1st hr
4th "	54.3 "	0.570	5th "	55.3 "	0.550	.020	5th "
8 " "	63.0 "	.408	9 " "	64.0 "	.393	.015	9th "
12 " "	71.5 "	.295	13 " "	72.5 "	.284	.011	13 " "
16 " "	80.0 "	.212	17 " "	81.0 "	.203	.009	17 " "
20 " "	88.5 "	.153	21st "	89.5 "	.147	.006	21st "
24 " "	97.3 "	.107	25th "	98.3 "	.102	.005	25th "
28 " "	105.5 "	.077	29 " "	106.5 "	.073	.004	29 " "
30 " "	109.6 "	.064	31st "	110.6 "	.062	.002	31st "

Π stands for emf, $\Delta \Pi$ for change in emf in our hour due to adsorption, and Δa is the change in activity in one hour due to adsorption.

The values of Π were obtained from Curve I. For example, the emf was 54.3 mv at the end of the 4th hour. During the 5th hour the emf will change 1.0 mv due to adsorption giving 55.3 mv. From the activity-emf curve the values of the ion activities corresponding to 54.3 and 55.3 mv are read off. This gives a and $a + \Delta a$, and by subtraction Δa is obtained. This gives the activity of chloride ion adsorbed

²⁵ Lewis and Randall—Thermodynamics, p.344 (1923)

during the 5th hour. These values of Δa were plotted as ordinates against their respective hours as abscissas. A smooth curve was obtained, in which no point deviated more than 0.002 millimole from the curve.

From this curve the total amount of chloride adsorbed at the end of any time was obtained by adding the ordinates. The total amount adsorbed in four hours, for example, was gotten by adding the amounts adsorbed during the 1st, 2nd, 3rd and 4th hours—these quantities being obtained from the curve of Δa against Time. These values are given in Table XIII.

TABLE XIII.—.0008 m.

Time	4 hrs	8	12	16	20	24	28	31 hours
Chloride Ion	.09	.16	.22	.26	.29	.31	.33	.34 millimoles
Adsorbed								per l.

These values are given graphically by Curve XI.

A similar procedure was gone thru from the data and curves on .001 molar. From the first parts of Curves IV and VI we get for .001 m.

$\Delta E.M.F. = 2.2$ mv per hour for electrolysis and adsorption.
and $\Delta E.M.F. = 1.2$ mv per hour for electrolysis alone.
giving $\Delta E.M.F. = 1.0$ mv per hour for adsorption alone.

From these were calculated Δa and the total a absorbed as was done for .0008 m. The following results were obtained:

TABLE XIV.—.001 m.

Time	4 hrs	8	12	16	20	25	28	35 hours
Chloride Ion	0.13	0.23	0.31	0.36	0.39	0.42	0.42	0.42 millimoles
Adsorbed								per l.

This is given graphically by Curve XII.

These two curves XI and XII confirm the hypothesis of Briggs and Davidson that the number of particles increases with prolonged arcing until a maximum is reached. Then the particles increase in size. It is seen that the slopes of these two curves decrease and finally flatten out. The .001 m. adsorption curve is higher than the .0008 curve, which confirms their hypothesis that there are more particles formed in solutions of higher electrolyte concentration.

Thus at .0008 m. almost all the chloride ion has disappeared, the activity decreasing from .00078 to .00007. Electrolysis accounted for about .0004 and of the remaining .0004 about .0003 has been adsorbed, less than .0001 remaining. At

.001 m. the activity decreased from .00098 to .00013. Almost .0005 was electrolyzed, about .0004 was adsorbed, leaving slightly more than .0001. Thus it seems that about 75 or 80% of the available chloride ion was adsorbed.

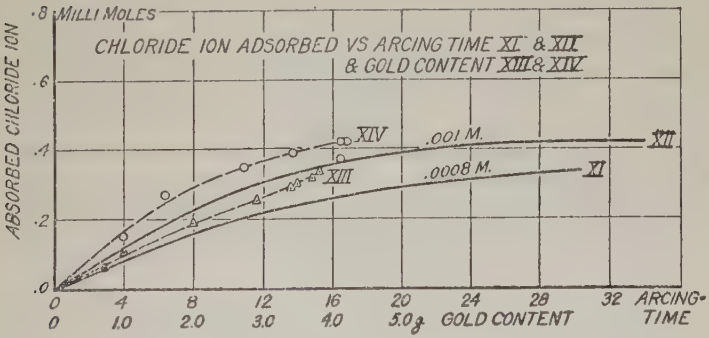
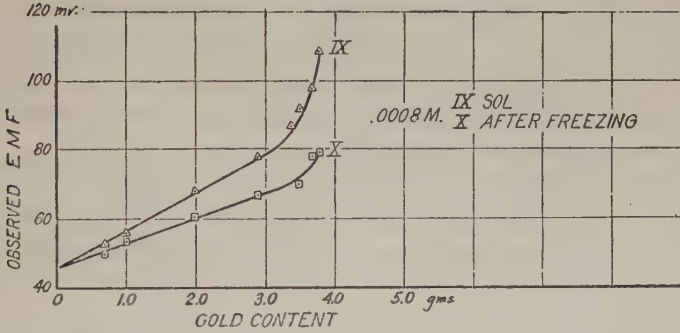
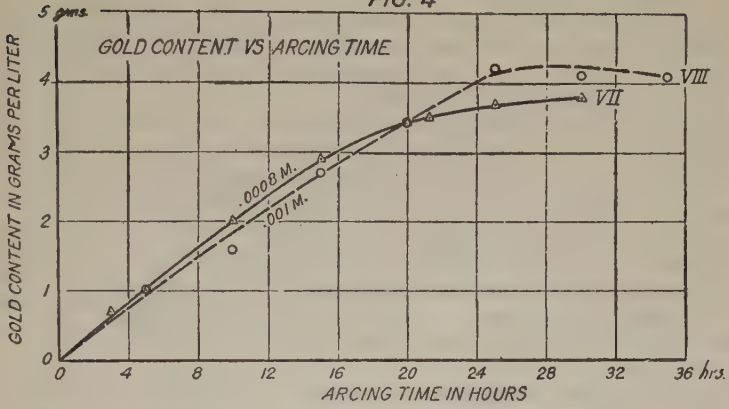
From these two curves the chloride adsorbed by each sol has been obtained, since the arcing time of each sol is known. Curves XIII and XIV give the relation between the gold content and adsorbed chloride ion for .0008 and .001 m. respectively. The number of gold atoms per chloride ion adsorbed at the maximum is for .0008 m

$$\begin{array}{rcl}
 \frac{3.8 \text{ gms gold}}{197.2} & \times 6.06 \times 10^{23} & \\
 \hline
 3.4 \times 10^{-4} & \times 6.06 \times 10^{23} & = 57 \text{ gold atoms.} \\
 \text{and for .001 m} & \frac{4.2 \text{ gms}}{197.2 \times 4.2 \times 10^{-4}} & = 51 \text{ gold atoms.}
 \end{array}$$

These values check well. They are probably low however, since the amount of colloidal gold has been obtained by analysis after 30 minutes centrifuging. Analysis before centrifuging leads to gross inaccuracies since the sol contains considerable suspended gold. Just where the dividing line between suspended and colloidal gold is to be drawn is at present an arbitrary matter. The only criterion we have at present of the stability of gold sols is the ability to resist settling under a normal or accelerated gravitational field. The strength of the field and the time involved are a matter of arbitrary definition at present. Thirty minutes was chosen here because deviations in starting and stopping the centrifuge cause relatively larger errors at smaller times of centrifuging.

Altho the observed emf in the sols was not constant, varying about one or two millivolts from the values given, yet the two electrodes in each sol almost always checked to better than one millivolt. When the emf of the cell drifted up or down, the two electrodes went up and down together, showing that the emf was being measured with precision, and that the changes in emf were due to changes occurring in the sol. The points do not deviate widely from the curves at .0008 m. at least, and $\Delta E.M.F.$ per hour for adsorption is estimated to be correct to about 0.2 mv per hour. These values have not been corrected for the solubility of AgCl since at .0001 m. the correction is only about .000002 and is less at higher concentrations, and the adsorption values are given here to hundredths of a millimole.

FIG. 4



While on the subject of precision, attention is drawn to the claims of Linhart¹⁸ who states he obtained "results of high precision nearly to a concentration of 0.0001 M." Now totally apart from the author's work with this electrode, and confining ourselves exclusively to the paper in question we see that Linhart gave seven results for as many different solutions. There were no check electrodes in any solution, and no solution was measured in duplicate. In other words the reproducibility of the electrodes is not given. In the absence of such data it is difficult to see how the precision stated was estimated. Even if the measurements agreed excellently with the values calculated on the basis of various theories, the conclusion to be drawn is that they agree with calculated values, but hardly that they have high precision. The method may really give results of high precision but that conclusion cannot be drawn from the seven experiments published.

As a matter of fact Linhart considered the measurement in the most dilute solution as too low, and discarded it. In addition Scatchard, using the gauze electrode, found²⁶ that there was a discrepancy between his results and Linhart's at 0.01 m. Scatchard made three measurements at this point and Linhart only one. Thus two out of the seven measurements are of doubtful accuracy.

In discussing the composition of gold sols reference has been made almost exclusively to the work done in this laboratory. This does not mean that other work has not been done. On the contrary there has been published a considerable mass of material on gold sols but it has been on poorly defined systems. For example, altho Svedberg has been aware^(2,27) of the very great influence of small additions of electrolytes on the formation of colloids, and of the very great importance of the kind of water used, yet neither he nor his students have taken the precaution of starting with water of known purity. Obviously since the nature and quantity of the impurity present in such work is unknown, nothing definite regarding the nature of colloidal gold can be deduced from their data.

Altho the conclusions drawn in this paper have been restricted to Bredig sols, yet it seems highly probable that gold

²⁶ Scatchard—J. A. C. S. 47, 644 (1925).

²⁷ a. Svedberg—Colloid Chem., p. 52, 58 (1924).

b. Borjeson—Diss. Upsala (1921), p. 63-4. "Bredig's method gives stable Cd-alcossols, but stable sols of Au could not be obtained either in alcohol or in pure water."

sols prepared without the use of an arc or spark have the same kind of composition. A large mass of literature has been accumulating on chemically prepared gold sols, but without exception the systems are loaded with relatively enormous quantities of electrolyte and often with organic matter also. Frequently a large portion of the electrolyte is dialysed out, but as a result of dialysis important changes often occur in the sols. In addition dialysis may introduce an unknown amount of organic impurity. As a result, it is not at all safe to apply to sols, theories based upon observations of systems that have undergone an unknown amount of alteration both physical and chemical.

If the gap between Bredig and chemical sols is to be bridged, the amount of electrolyte in the system must be a known small quantity. Some work along this line has been done in this laboratory. Starting with water of a definite low conductivity, a suspension of purified gold oxide was added to it and then hydrogen gas was bubbled thru. Encouraging results were obtained, but before anything definite can be said, the exact amount of electrolyte impurity in the gold oxide must be determined. As yet this has not been done.

Another possible way of attacking this problem without loading the solutions with large quantities of extraneous material is that of some modification of the method of Furth.²⁸ Altho his method failed in the case of gold, it may have been due in part to the fact that he used "water." He too overlooked the necessity for electrolyte.

As regards the sols made in the usual chemical ways, there is as stated above, a tremendous amount of electrolyte present. Dialysis removes electrolyte, but the systems prepared in this way are so complicated and have undergone such changes that any conclusions from them regarding the constitution of colloidal gold are more of the nature of guesswork than of definite knowledge.

In addition to loading up the solution with all sorts of substances all the investigators with but one exception have started with contaminated water. That exception is Hiege, one of Zsigmondy's students, who studied²⁹ the effect upon the formation of gold sols of adding various substances before reduction. He found that there was a marked difference in the properties of the sol if he used carefully redistilled water instead of ordinary water.

²⁸ Furth—K. Z. 34, 224 (1924).

²⁹ Hiege—In. Diss. Gottingen (1914).

The complicating effect of the substances usually used in the reduction can be seen when his findings are examined. He found that addition of small quantities of KNO_3 or K_2SO_4 to the purified water before reduction had a harmful effect. The effect of KCl , KBr , and KI , he also considered harmful altho he noticed that their first effect was beneficial. The systems he studied were so complex that the correct estimate of the importance of particular anions was lost on him.

In view of the fact that chemical gold sols are of the ill-defined nature described above, the validity of conclusions regarding the structure of colloidal gold from such data are not comparable with the validity of conclusions drawn from the systems studied in this laboratory. However, since Pauli and his co-workers have presented a theory which is similar to ours their theory will be briefly discussed.

According to Kautzky and Pauli³⁰ and to Adolf and Pauli²⁵ colloidal gold is not a suspension of simple pure metal particles. The colloidal particle, they say, is composed of metallic gold with an adherent complex gold compound which ionizes, giving off a positive ion, and leaving the particle negatively charged. They conclude that the complex ion adsorbed is an aurate of same sort.

Altho their conclusion that the particles have adsorbed a negative ion agrees with ours, their evidence as to the nature of this ion is weak. It is based largely upon analogy with the hydrophile systems studied there, upon chemical analysis of the precipitated gold, and upon emf measurements on the filtrate after the sol has been precipitated and filtered off.

Without going into great detail it is pointed out that the gold sols were precipitated by addition of electrolytes and analyzed. Even if the sols had been precipitated by freezing, without adding any additional electrolyte, chemical analyses of the gels from such sols would not give data of sufficient reliability to warrant conclusions as to molecular structures. Neither do emf measurements of the concentration of the contra-ion on the filtrates from such sols, give any information regarding the nature of the adsorbed ion. Certainly reasoning by analogy from systems as different from gold sols as ferric oxide sols, cannot be admitted as evidence.

The phenomena observed by them can be easily explained on the basis of our theory, while their theory cannot explain our results. When they find chlorine in the gel, it is not because there was adsorbed a hypothetical complex chlorauric acid, but because simple chloride ion was adsorbed.

³⁰ Kautzky and Pauli—Kollch. Beih. 17, 295 (1923).

Their theory cannot explain why the Bredig method fails in water while it is successful in dilute chloride and hydroxide solutions.

Attention is drawn to the fact that Mellor's summary³¹ of the results of Beans and Eastlack is somewhat misleading. He states that these authors "believe that an oxide of the metal is formed and adsorbed during the sparking. The negatively charged platinum, gold, etc. are much more stable if chlorides, bromides, iodides or hydroxides are present." In the case of gold, no oxide was observed; in the case of platinum it was probable that oxidation of platinum to ionic form occurred; no oxide was observed with platinum either. It is not that gold is more stable if the above anions are present, but that a sol is impossible if they are not present.

VIII. Conclusions.

By means of emf measurements it has been shown that electrolysis of chloride ion occurs in dilute KCl solutions, resulting in a decrease in chloride ion activity, when direct current is used under conditions similar to preparation of Bredig gold sols. When Bredig gold sols are prepared in KCl solutions, emf measurements show a larger decrease in chloride ion activity. The precision of the method and the reproducibility and regularity of the results are such as to show clearly that electrolysis cannot account for all the chloride ions lost. In the light of earlier researches in this laboratory, it has been concluded that the difference between the total chloride ion decrease, and the decrease due to electrolysis, is due to adsorption of chloride ion by the gold.

Freezing a gold sol precipitates the gold and breaks up the complex with liberation of chloride ion. All of the chloride previously bound up is not released however; the difference is probably carried down by the precipitated gold. Centrifuging causes additional adsorption of chloride ion.

Ionic changes occur in the sol on standing. These are probably due to changes in the equilibria of the oxidation products of the electrolyzed chloride and may also be due in part to changes in the gold complex. Suggestions for avoidance of the complicating effects of the former have been made.

From the data obtained it has been calculated that at about the maximum gold content, there are about 54 gold atoms to every chloride ion adsorbed.

Since chloride ion disappears on formation of colloidal gold and reappears on the destruction of the sol by freezing, Beans and Eastlack's complex theory of Bredig gold sols is regarded as conclusively proved.

³¹ Mellor—Ibid III, p. 540.

IX. Summary

1. The silver chloride electrode of Linhart has been found unsatisfactory in gold sols.

2. The gauze electrode of MacInnes and Parker has been found satisfactory in dilute potassium chloride solutions, emfs being measurable with a precision of one millivolt.

3. Emf measurement have been made with the gauze electrode in Bredig gold sols with a precision of one millivolt.

4. The chloride ion activity in a gold sol is considerably less than that in the solution from which it was made; in .0008 m. KCl the activity decreased from 0.00078 to 0.00007; in .001 m. KCl, from 0.00098 to 0.00013.

5. Electrolysis of chloride ion occurs during arcing. This accounts, however, for only a part of the decrease in chloride ion activity.

6. Centrifuging the sol produces a further decrease in chloride ion activity.

7. Precipitation of the sol by freezing causes an increase in chloride ion activity.

8. The amount of chloride ion released on the breaking of the complex is a large fraction of the total amount of chloride originally adsorbed by the gold.

9. The results obtained in this research are in accord with the findings of the previous investigators working in this laboratory.

10. The complex theory of gold sols advanced by Beans and Eastlack in 1915, and firmly established by subsequent workers in this laboratory, is now conclusively proven by direct evidence.

VITA

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